I. OZONIZATION STUDIES ON POLYBUTADIENE STRUCTURE

II. OPTICALLY ACTIVE RESINS FOR CHROMATOGRAPHY

BY

CLAIRE SYLVIA KRAIMAN BLUESTEIN

A.B., University of Pennsylvania, 1947
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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I. OZONIZATION STUDIES ON POLYBUTADIENE STRUCTURE

Introduction

The purpose of this research was to study a series of polybutadienes, in which only the degree of conversion varied, by a standard oxidative ozonolysis procedure to see if the method would reveal significant structural differences.

Previously, polybutadienes and other synthetic rubbers have been studied by ozonization procedures, but due to the difficulty of separation of the products formed, only the major components of the mixture were identified. The recent development of an efficient system of separation for organic acids by partition chromatography (1) makes it possible to isolate and identify many more of the degradation products.

A study was planned to find evidence on whether the presence of tricarballylic acid in mixtures obtained through ozonolysis and oxidative cleavage (2) was indicative of chain growth in the polymer by a process called branching. Branching takes place if there arises a free radical in an allylic position along the polymer chain formed by ordinary addition of butadiene. The free radical then adds to other butadiene molecules, with subsequent chain lengthening in another direction.

Discussion of Results

Polybutadienes prepared at 50° to conversions of 20.0, 40.0, 60.5, 81.0 and 97.0 per cent were examined by an ozonization procedure which consisted of purification, ozonolysis with 2 per cent ozone, oxidative cleavage with 3 per cent hydrogen peroxide and examination of the resulting acid mixture by partition chromatography.

By comparison of the ratios of succinic acid to β-carboxyadipic acid, the two major components of the mixture, it was noted that the ratio for the 20.5 per cent conversion was higher

than that for the 97.0 per cent conversion, but the lowest value was obtained for the 60.5 per cent conversion rubber. This ratio is a quantity which indicates the amount of 1,4-addition versus 1,2-addition of butadiene. The same trend was duplicated in a second series of determinations in which the only difference was that the hydrogen peroxide treatment was carried out under more vigorous conditions.

In the second series of determinations, tricarballylic acid was found in every rubber, whereas it was not found at all in the first. Further oxidations of mixtures obtained from the first determinations did not yield tricarballylic acid when sodium dichromate, periodic acid and iodic acid were used, but did when 6 per cent hydrogen peroxide and silver oxide were used. It can be concluded that tricarballylic acid is largely a secondary degradation product.

Attempts, by large scale separation of the mildly oxidized mixtures, to isolate the substance which could be oxidized to tricarballylic acid revealed that there were several, of which each was a complex material whose nature could not be elucidated. Other unexpected acids found were acetic acid, β-formylpropionic acid and levulinic acid.

The mixtures always yielded considerable amounts of carbonyl compounds, which could be isolated as their 2,4-dinitrophenylhydrazones. The hydrazone mixture was found to be seperable on an adsorption column of 2:1 silicic acid- celite. In addition to derivatives of the acids with carbonyl groups mentioned above, the 2,4-dinitrophenylhydrazones of acetone, acetaldehyde, β-formyladipaldehyde and others which were not completely characterized were isolated.

II. OPTICALLY ACTIVE RESINS FOR CHROMATOGRAPHY

Introduction

Resolution of racemic mixtures into their optically active

components has been accomplished by chromatographic adsorption on *d*-lactose hydrate. *p*-Phenylene bis-iminocamphor (3) and Tröger's base (4) were resolved this way.

In order to extend the utility of this procedure, the synthesis of optically active polymers of different chemical types, which would have suitable properties for adsorbents, was planned.

Discussion of Results

Preliminary trials were conducted with cellulose to find if *dl*-phenylsuccinic acid could be resolved chromatographically. The resolution failed when any of several different methods of activation of the cellulose and different solvents were used.

The preparation of polyesters of *d*-tartaric acid with ethylene glycol and glycerol was attempted. The ordinary methods yielded discolored, degraded substances, which were completely insoluble except in sodium hydroxide with decomposition.

An optically active phenol was prepared by condensation of *l*-β-pinene with phenol. However, the preparation of polymers by condensation of formaldehyde with a "pinyl" phenol (5) with both acid and basic catalysts showed that this type of resin was unpromising as a chromatographic adsorbent. They were soluble in organic solvents and very water repellant.

A very insoluble polymer was prepared from *l*-α-aminophenylacetamide and formaldehyde. This material is probably similar to urea-formaldehyde type resins (6). It appears potentially useful as a chromatographic adsorbent.

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VITA

The author was born in Philadelphia, Pennsylvania on May 3, 1926. She attended the public schools there, graduating from Simon Gratz High School in February, 1944. Her education was continued at the University of Pennsylvania, from which she received a Bachelor of Arts with Honors in Chemistry in June, 1947. At that time, also, she was married. She entered the Graduate College of the University of Illinois in September, 1947 with a University Fellowship which lasted until June, 1948. She was a research assistant on the WPB Rubber Research project from February to August, 1950.

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